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An Evaluation of Certain Methods For the Chemical Analysis of Styrene-Butadiene Rubber



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An Evaluation of Certain Methods for the Chemical Analysis of Styrene-Butadiene Rubber

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An Evaluation of Certain Methods for the Chemical Analysis of Styrene-Butadiene Rubber

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Abstract

The applicability of available methods for the analysis of unvulcanized styrene-butadiene rubber (SBR, formerly GR-S) for organic acid and soap is influenced by the type of coagulation (alum or salt-acid), the type of acid present (fatty acid, rosin acid, or mixed acids), and the presence of carbon black or oil. No single method is universally applicable for the analysis of organic acid and soap, but reasonably unbiased results can be attained by proper selection of the available procedures.

The complete-solution procedure for alum-coagulated (AC) SBR has given reasonably good results for organic acid in samples containing mixed acids, while the extraction procedure using aqueous isopropanol-toluene azeotrope (ITA) gives good results for AC samples containing fatty acid only.

The complete-solution procedure for SBR coagulated with salt and acid gives less biased results for organic acid and soap than the aqueous ITA extraction procedure, but the latter should be used for all SBR containing carbon black and for estimating oil in oil-rubber masterbatches. Both complete-solution procedures and the ITA extraction procedure can be adapted for the determination of stabilizer and bound styrene. The present ASTM extraction procedure using ethanol-toluene azeotrope is less satisfactory than the other procedures.

Key words: Bound styrene; carbon black; chemical analysis; latexes; oil; organic acid; serums; soap; stabilizer; styrene-butadiene rubber (SBR); washes.

1. Introduction

A knowledge of the chemical constituents of styrene-butadiene rubber (SBR, formerly GR-S) is useful in maintaining uniformity of production. Some of the constituents of principal interest are organic acid, soap, bound styrene, and stabilizer.

The nature of some of the constituents depends on the method of coagulation used in preparing the rubber. One method uses salt (sodium chloride) and acid (sulfuric acid) to produce salt-acid (SA) coagulated rubber. A second uses "alum" (aluminum sulfate) as coagulant for alum-coagulated (AC) rubber. Sodium or potassium soap is used in the polymerization process. The SA rubber contains organic acid derived from partial neutralization of the soap. It should also contain a relatively small amount of unreacted soap. Alum-coagulated rubber, however, presumably contains, as aluminum soap, free and bound organic acid, and perhaps some unreacted sodium or potassium soap. Materials balance studies involving the comparison of the amount of organic acid in the soap that goes into making AC rubber and that found on analysis by the present ASTM procedure (1)¹ employing aqueous ethanol-toluene azeotrope (ETA) indicate that this procedure gives low results. Since a similar ASTM method using anhydrous ETA to extract sodium soap and organic acid from SA rubber (1) gives much more consistent materials balance figures, the difficulty encountered in the analysis of AC rubber is probably due to the presence in the rubber of aluminum soap that is not readily extracted. Anhydrous ETA is even less effective than aqueous ETA for extracting AC rubber. The water present in the latter solvent aids in the hydrolysis of the aluminum soap and thus in the subsequent extraction of the organic acid.

Three other methods besides the ASTM procedure using aqueous ETA have been suggested for the analysis of AC rubber. The ASTM procedure involving the use of anhydrous ETA for the analysis of soap and organic acid in SA rubber, although much less biased than the method for AC rubber, is not completely satisfactory either. Consequently, two other methods for SA rubber have been suggested.

This paper deals largely with a comparison and evaluation of these seven methods. The ASTM methods for stabilizer and bound styrene are free of detectable systematic errors

¹The italic numbers in brackets refer to the list of references appended to this paper.

but require separate specimens. It would be convenient to run these tests on the same specimens used for the organic acid and soap determinations. Methods evaluated here that were useful for organic acid and soap have therefore also been adapted for the determination of stabilizer and bound styrene and checked for systematic errors by comparison with the ASTM procedures. Several new methods of analysis necessary for the evaluations have been developed and are also presented, along with improvements for two of the suggested procedures.

2. Samples

For the purpose of evaluating the systematic errors in methods for soap and organic acid in AC rubbers, pairs of samples of SA and AC rubber were coagulated from the same latex. The SA samples are also used for evaluating methods for SA rubber relative to an unbiased complete-solution (CS) procedure for this type of rubber (2).

Two sets of samples were specially prepared by each of three different collaborating plant laboratories. A complete set consisted of an AC and an SA sample prepared from a single latex, the latex itself, and the respective serums and washes. These samples are described in Table 1. The preparation of the two sets of samples GG-1 and GG-2 was repeated, because of conflicting results obtained by the CS procedure for AC rubber, using new latexes and producing samples GG-1 N and GG-2 N. In addition, Phillips Petroleum prepared a sample containing carbon black (designated 6608P) and a solution polymer (Solprene 1205), both containing soap, that were used in comparing the performance of indicators.

3. Organic Acid and Soap in SA Rubber

3.1 Methods Evaluated

3.1.1 ASTM ethanol-toluene azeotrope (ETA) extraction procedure (ASTM D 1416, Sections 30-40) (1).

Six grams of thinly sheeted sample is extracted with two 100-ml portions of solvent and the combined extracts made up to 250 ml. One-hundred ml aliquots are titrated for soap and organic acid, respectively, using m-cresol purple as indicator in both titrations.

3.1.2 Isopropanol-toluene azeotrope (ITA) extraction procedure (3).

ITA containing 8 percent by volume of H₂O is used in place of anhydrous ETA in the ASTM procedure.

3.1.3 A complete-solution (CS) procedure (2).

Five grams of sample is dissolved in 5:1 toluene-absolute ethanol, the solution is made up to 250 ml, and aliquots are used for the determination of organic acid and soap.

3.2 Detection of Systematic Errors

The CS procedure for SA samples has been evaluated and found free of detectable systematic error (4). Method 3, therefore, is the standard against which methods 1 and 2 are evaluated.

3.3 Results and Discussion

The CS procedure eliminates the difficulty of incomplete extraction inherent in the extraction procedures, but cannot be used for the analysis of SBR containing carbon black that gives a colorimetrically untitratable opaque solution. Extracts of SBR containing carbon black, on the other hand, can be titrated colorimetrically. The estimation of oil in oil-rubber masterbatches similarly requires an extraction procedure.

The results of the analysis by the three methods of the eight SA samples are given in Table 2. Each value represents at least two but usually four to six determinations. The results for organic acid tend to run low for the extraction procedures and on these samples may be low by as much as 0.3 percent for the ITA procedure and 0.23 percent for the ETA procedure. Of the samples containing large amounts of soap (over 1 percent) the extraction procedures give quite low results for this constituent. Somewhat better results are obtained on samples containing the usual amount of soap, 0 - 0.75 percent. One (PP-2 SA) is low in soap content by 0.16 percent by the ITA procedure, and one (F-1 SA) low by 0.20 percent by the ETA procedure. Table 3 shows that for both tests most of the differences are statistically significant and that the biases are approximately the same for the ITA and ETA methods.

Since the systematic errors in the ETA procedure are as great as those in the ITA procedure and since, as demonstrated below, the ITA procedure will have to be used for some AC samples, it would simplify matters to eliminate the ETA procedure from further consideration. In Table 4, which covers more completely the usual range of soap concentrations, a further comparison is made of a number of samples analyzed by the CS and ITA procedures. Each value in Table 4 represents at least two determinations. The extraction

procedure in this series of tests gives results that are low by as much as 0.14 - 0.16 percent. The differences for the last three samples are all statistically significant.

3.4 Conclusions

The CS procedure is the most reliable method for organic acid and soap in SA rubber and should be used for all samples except those containing carbon black or oil. The ITA procedure should be used in these latter cases. Since the ITA and ETA procedures are equivalent for SA rubbers, and since ITA is preferred over ETA for AC rubbers, ETA should be omitted from further consideration.

4. Organic Acid and Soap in AC Rubber

4.1 Methods Evaluated

4.1.1 Aqueous ETA extraction procedure (ASTM D 1416, Sections 30-40 (1)).

This is the same as Method 1 for organic acid and soap in SA rubber, except that 5 percent by volume of water has been added to the ETA to hydrolyze the aluminum soap.

4.1.2 Acetic acid-ETA extraction procedure (5).

This procedure, modified slightly in the present application, involves extraction with ETA containing 5 percent by volume of glacial acetic acid to convert the aluminum and sodium soaps to organic acid. The rubber is washed with ETA and the washings added to the extract. The acetic acid is then removed by extraction with water after the addition of n-hexane to the extract. After partial evaporation of the organic solvent, isopropanol is added and the titration made with 0.05 N aqueous sodium hydroxide, using phenolphthalein as indicator. The modifications involve washing the extracted rubber with ETA instead of n-hexane, which dissolves the rubber, testing the last water wash for acidity with litmus, and using isopropanol instead of methanol to reduce the size of the blank.

4.1.3 Aqueous ITA extraction procedure.

ITA containing 8 percent by volume of water (3) is substituted in the present method for ETA in the ASTM procedure (1) instead of being used in the manner originally described (3).

4.1.4 A complete-solution procedure (6).

The rubber is dissolved in toluene, the aluminum ion is complexed with 8-hydroxyquinoline, and 95 percent ethanol is added before titration of the organic acid with alcoholic sodium hydroxide, using m-cresol purple as indicator and employing a colorimeter to follow the course of the titration.

4.2 Systematic Errors

The organic acid content of AC samples, including that which may be present as soap, must be determined indirectly as follows:

4.2.1 By comparing the organic acid content of the latex before coagulation with that in the rubber, serum, and wash water after coagulation, including that present as soap. When rubber is coagulated from latex, the liquid portion or serum which remains may contain a trace of soap or organic acid. Another trace of soap or organic acid may be lost from the rubber to the water with which it is washed. Usually the organic acid in washes and serums amounts to less than 0.1 percent of the rubber, but for a strict accounting of all of the soap and organic acid originally in the latex, these traces must be determined and added to that in the rubber. This grand total will be referred to as total organic acid.

4.2.2 By comparing the total organic acid content of the AC sample with that of an SA sample coagulated from the same latex. For this purpose, the organic acid and soap contents of the SA sample are determined by the CS procedure for this type of rubber (2), which is known to be unbiased (4). Subtracting the organic acid found in the AC washes and serums from the total organic acid content of the SA sample should give the true organic acid content of the AC rubber. For comparison, the organic acid and soap contents of the AC sample would be determined as directed by each of the methods under question.

4.3 Results and Discussion

All of the results present in Tables 5 and 6 represent averages of at least two but usually three to six determinations.

The results of tests for total organic acid in samples from all three plant laboratories are presented in Table 5. Values for the CS procedures for AC and SA rubber, the aqueous ITA extraction procedure, and the ASTM ETA extraction procedures (1) are given along with values for the organic acid contents of the latexes. The latexes, washes and serums

of these samples were analyzed by methods given later in this paper.

It was found that some of the AC samples contained traces to appreciable amounts of titratable base (if calculated as organic acid, up to 16 percent of the organic acid present), which was assumed in the calculations for total organic acid in the ITA and ETA analyses to be sodium soap. As will be seen from the data, the extraction methods generally give low values, presumably because of incomplete extraction.

A comparison is made of the total organic acid content of each AC sample, including serum and washes, with that of the corresponding SA sample analyzed by the CS procedure. In most cases the organic acid content of the latex is somewhat higher than the total organic acid in the rubber, serum, and washes determined by the CS procedure on the SA sample. This fact suggests that something may be lost in accounting for the organic acid in the serum and washes. Since this is possible for AC and SA rubbers alike, a comparison of the total organic acid content of the AC rubber with that of the SA rubber seems to be more valid than the same comparison of the AC rubber with the latex. In any event, the difference between the two comparisons is not excessive.

It will be noted in Table 5 that none of the methods gives consistently good results on all of the AC samples, with the ETA extraction method coming out a poor third.

Overall, the ITA extraction procedure gives better results (0.18 percent low on the average) than the CS procedure (0.51 percent high on the average) for the AC samples containing fatty acid alone. It should be noted that the CS procedure gives very good results for samples F-1 AC and F-2 AC and high results on GG-1 AC and GG-2 AC and the repeated samples GG-1 N AC and GG-2 N AC.

If it is assumed that these samples are typical of production containing fatty acid only, 95 percent confidence intervals can be calculated for the average systematic error of both methods. These confidence intervals do not overlap. The one for the ITA procedure just includes zero difference at the lower end of the interval, and the one for the CS procedure is, of course, on the other side of zero and does not include zero. On this basis, it is reasonable to infer that results obtained with the use of the ITA procedure will have smaller systematic errors than with the CS procedure.

Further evidence was obtained supporting the use of the ITA procedure for AC samples containing fatty acid only. Of these samples, one, GG-2 AC giving high, and one, F-2 AC giving satisfactory results by the CS procedure, were analyzed by the acetic acid-ETA extraction procedure (5). Both samples gave results about 0.3 percent low by this method, values which were comparable to those obtained with the ITA extraction procedure. Since the method employing acetic acid should completely convert the aluminum soap to organic acid and provide good results, these data lend support to the use of the ITA method for AC samples containing fatty acid only. The acetic acid method is, of course, too time consuming and cumbersome to be considered for routine use.

On the other hand, very poor results are obtained by the ITA procedure on the two samples containing mixed acids. The CS procedure fares better on these samples, giving results only 0.52 percent low in comparison to those 1.55 percent low for the ITA procedure. These former results are, however, erratic. The comparison of the results is more readily seen in Table 6.

4.4 Conclusions

A considerable portion of SBR contains rosin acid. Further work on samples containing rosin or mixed acids is needed to verify whether the difference in behavior is actually due to the type of acid present. Until this research is done, the two methods (CS and aqueous ITA) should be used on the samples for which they are better suited. Again, the ITA procedure must be used for estimating oil in oil-rubber masterbatches and for analyzing samples containing carbon black.

5. Stabilizers and Bound Styrene by ITA Extraction Procedure

5.1 Methods

5.1.1 Stabilizers

Samples containing PBNA,² BLE,³ or Stalite⁴ may be analyzed for stabilizer content by ultraviolet absorption measurements as in the ASTM extraction procedure (ASTM D

²Phenyl-beta-naphthylamine

³Reaction product of acetone and diphenylamine

⁴Mixed alkylated diphenylamines

1416, Sections 49-54, Method B (1)) by diluting a 2 ml aliquot of the aqueous ITA extract to 100 ml with 85:15 methylcyclohexane-isopropanol spectrograde solvent mixture. The reference solutions for calibration are made by dissolving 0.03 g of stabilizer in 100 ml of aqueous ITA and taking three 2 ml aliquots, which are diluted to 100 ml with the same spectrograde solvent mixture. This mixture has a transmittance of 98.5 percent or better at 288 and 309 μ , where the measurements are made. As implied in the ASTM procedure, nonspectrograde solvents should be satisfactory if the transmittance of the mixture is greater than 90 percent.

5.1.2 Bound Styrene

Alum-coagulated and SA samples may be analyzed for bound styrene content by a modification of the ASTM procedure (ASTM D 1416, Sections 25-29 (1)). A small piece of the extracted 6 g sample suitable for use in the ASTM procedure is pressed between sheets of aluminum foil about 2.5 inches on a side in a laboratory press. The aluminum sheets are pulled apart with a clean continuous pull, and the rubber adhering to one sheet of the foil is dampened with a little isopropanol to facilitate removal as a thin film. The thin film (about 0.004 to 0.01 inch in thickness) is then extracted for 15 min with 60 ml of aqueous ITA for the SA samples or anhydrous ITA containing 1 percent of concentrated hydrochloric acid for the AC samples. The small specimens are then treated according to the ASTM procedure and the bound styrene content determined from the refractive index.

5.2 Results and Discussion

5.2.1 Stabilizer

The results of analyses for stabilizers in AC and SA rubbers by the ITA method are presented in Table 7, along with values obtained by the ASTM complete-solution procedure (ASTM D 1416, Sections 42-48, Method A (1)). The latter should give unbiased results, since in this procedure the whole sample is dissolved and an adequate correction is made for the absorption of the rubber itself. Each value represents an average of at least six measurements on each of two or three different specimens. Unbiased results are obtained by the extraction procedure for PBNA, somewhat low results for Stalite, and quite low results for BLE. The reason for the difference between the stabilizer contents of SA and AC samples coagulated from the same latex is not clear.

5.2.2 Bound Styrene

The results of the bound styrene analyses are given in Table 7, along with values obtained using the two 1-hour extraction periods with the small untreated specimens as required by the ASTM procedure (1), which is known to give unbiased results (7). Each value represents an average of at least six determinations on each of two or three specimens. The present method may be considered satisfactory. This procedure affords some saving of time in comparison with the ASTM procedure and avoids duplication of extracting equipment.

The extra extraction on the small sheets of rubber that is recommended in this procedure is necessary to give unbiased results, presumably because of occlusion of materials in the 6 g samples. For example, without this additional treatment, values obtained on one AC sample were low by as much as 0.82 percent, with differences between specimens from a single sample as great as 0.29 percent. Salt-acid coagulated samples can run 0.50 percent low with similarly poor precision. Of course, this method cannot be used with carbon black masterbatches.

5.3 Conclusions

The ITA extraction procedure for stabilizers is unbiased for PBNA, approximately unbiased for Stalite, and poor for BLE. For bound styrene determinations, the ITA procedure is quite satisfactory. It should be noted that the CS procedure for SA samples has also been adapted for the unbiased determination of any of the three stabilizers and bound styrene on a single specimen.

6. Thymol Blue as Indicator for Soap and Organic Acid in Aqueous ITA Extract

6.1 Methods

The indicator is prepared by dissolving 0.06 g of thymol blue in 6.45 ml of 0.02 N aqueous sodium hydroxide and diluting to 50 ml with distilled water. The color changes are from yellow to pink on titrating for soap with hydrochloric acid and from yellow to purple on titrating for organic acid with sodium hydroxide.

It is suggested that of the 250 ml of aqueous ITA extract, a 100 ml aliquot be used for organic acid, a 2 ml aliquot for stabilizer and the remaining 148 ml for soap, instead of the 100 ml used in the ASTM procedure. Ten drops of the indicator should be used for each 100 ml of solution.

6.2 Results and Discussion

Table 8 gives results obtained by using both thymol blue and m-cresol purple on 100 ml aliquots of the same aqueous ITA extract for both soap and organic acid. The samples were chosen so as to cover the usual range of soap and organic acid contents. It is apparent that essentially the same results are obtained in both tests for both indicators. Occasional high results for soap with m-cresol purple are attributed to the difficulty of detecting the end-point in this titration. Note the consequent poor precision in these cases. Thymol blue gives a satisfactory color change even in the presence of BLE, the most highly colored of the materials likely to be encountered in these extracts.

6.3 Conclusions

Thymol blue gives a more readily discernible end-point for soap titrated in aqueous ITA than does m-cresol purple, used in the comparison study. It is equally good for the titration of organic acid in this solvent.

7. Analytical Techniques for Organic Acid in Fluids

Methods have been devised for the determination of organic acid in latex, serums, and washes.

7.1 Latex

7.1.1 Method

A sample containing about two grams of solids is evaporated nearly to dryness at room temperature and to constant weight under vacuum at 120°C, and dissolved in 100 ml of 5:1 toluene-absolute ethanol. This solution is first titrated with 0.1 N alcoholic hydrochloric acid to the first permanent pink coloration, using m-cresol purple as indicator, then back titrated to the first permanent purple coloration with 0.1 N alcoholic sodium hydroxide. The organic acid content of the solids is calculated from the number of milliequivalents of sodium hydroxide consumed between the pink and purple end-points, with a correction for the appropriate blank.

7.1.2 Discussion

The titration of organic acid in a 5:1 toluene-ethanol solution of dried latex should give unbiased results when m-cresol purple is used as the indicator in the titration with sodium hydroxide (4). However, if organic acid is determined by first titrating the solution with hydrochloric acid to convert soap to organic acid, and then back titrating

with sodium hydroxide, using m-cresol purple in both cases, different results are obtained in the two directions, depending on whether excess base or acid is present in the latex. Since hydrochloric acid neutralizes excess base as well as converting soap to organic acid, it is necessary to determine organic acid solely by means of the back titration with sodium hydroxide. In the studies for systematic errors in the soap titration using m-cresol purple in 5:1 toluene-ethanol solutions of SBR (2, 4), the larger quantities of soap present in latex were not studied. Consequently, using a previously published plan (4), a study has been made of the systematic errors in the titration of these larger quantities of a fatty acid soap approximating sodium stearate in composition to determine the correctness of the starting point in the back titration with sodium hydroxide.

Selected known amounts of soap of known composition covering the range in question equivalent to 0.0 - 7 percent of the dried latex were dissolved in 5:1 toluene-absolute ethanol and titrated with alcoholic hydrochloric acid. The data were analyzed statistically. Table 9 gives the slope of the regression line as ml of hydrochloric acid per gram of soap (ml/g) and the intercept as ml of hydrochloric acid. These are compared respectively with the titre of the soap determined from its composition and with the experimental blank. Relative and constant type errors are assumed to be absent from the analysis if the resulting differences are insignificant in relation to the standard error of the slope and intercept, assuming that the calculated slope and experimental blank were determined with sufficient precision to be without error. In this case there is no evidence of either relative or constant type errors and the end-point in this titration should be a valid starting point for the back titration with sodium hydroxide.

7.2 SA Serums and Washes

7.2.1 Method

Approximately 100 g of serum or wash, weighed to the nearest 0.1 g, is acidified with 0.1 N hydrochloric acid. A 20 ml excess of the acid is then added to convert the soap completely to organic acid. The sample is extracted three times with 100 ml portions of ether. The combined ether extracts are washed free of mineral acid with at least three 50 ml water washes and evaporated to dryness on a steam bath. The residue is taken up in 100 ml of 5:1 toluene-absolute ethanol and titrated with 0.1 N alcoholic sodium hydroxide, using m-cresol purple as indicator. Organic acid in the total serum or wash is calculated as a proportion of the weight of the dried rubber obtained on coagulation plus the organic acid obtained from the serum and wash.

7.2.2 Discussion

Additional extractions with ether beyond the three indicated earlier did not yield additional organic acid; extraction using the indicated method is therefore complete. Since m-cresol purple gives good results in this solvent (4), the overall method should be unbiased. It has been shown that the absence of a pink color in the presence of m-cresol purple at the beginning of the titration verifies that free mineral acid had been removed from the ether by the water washes (2).

7.3 AC Serums and Washes

7.3.1 Method

A 100 g sample of serum or wash is weighed to the nearest 0.1 g in a 250 ml beaker, and the water is removed by evaporating the solution at the boiling point until 20 - 30 ml remain. It is then dried at about 50°C. The residue is taken up in 125 ml of toluene, and the aluminum is complexed with 8-hydroxyquinoline, using the same amount as in the CS procedure for alum-coagulated SBR. After adding 30 ml of 95 percent ethanol, the sample is titrated with 0.1 N sodium hydroxide according to that procedure but using 0.02 ml increments of base over the middle course of the titration to avoid over titrating the end-point. Organic acid in the total serum or wash is calculated as a proportion of the weight of the dried rubber obtained on coagulation plus the organic acid obtained from the serum and wash.

7.3.2 Discussion

A study similar to that made with sodium stearate has been made with an aluminum soap of known composition. The weighed samples covering the small concentrations encountered in the analysis of serums and washes (0 - 2.5 mg) were dissolved in toluene and treated and analyzed for organic acid in the manner described for AC serums and washes. A similar study was made covering the concentration range involved in the analysis of the AC rubber (as much as 130 mg). The results of the statistical analysis of these data are given in Table 9. There is no evidence of either relative or constant type errors in the method as applied to either range.

Since only quite small quantities of organic acid are found in the analysis of serums and washes, large positive errors such as those observed earlier with the rubber itself are not encountered. Furthermore, a green color is produced when aluminum soap is treated with 8-hydroxyquinoline. In the analysis of the serums and washes, this color developed

only when detectable amounts of organic acid could be titrated. Alum itself does not react to give this color with 8-hydroxyquinoline in the solvent used here. Thus the green color indicates the presence of aluminum soap and the titration should give the amount of organic acid present in the soap. Any unbound organic acid must also be accounted for at the same time.

The fact that large errors, either negative or positive, can occur when the method is applied to rubber itself, as shown in Table 5, suggests the presence of interfering conditions or substances not present in the aluminum soap used in the study of systematic error.

8. Summary

Organic acid and soap determined by the complete-solution procedure for styrene-butadiene rubber (SBR) coagulated with salt and acid exhibit smaller systematic errors than when the aqueous ITA extraction procedure is used. However, the aqueous ITA extraction procedure should be used for all SBR containing carbon black and for estimating oil in oil-rubber masterbatches.

The complete-solution procedure for alum-coagulated (AC) SBR has given reasonably good results for organic acid in samples containing mixed acids, while the extraction procedure using aqueous isopropanol-toluene azeotrope (ITA) gives good results for AC samples containing fatty acid only.

Both of the complete-solution procedures and the ITA extraction procedure can be adapted for the determination of stabilizer (except that BLE is low by 0.4 percent for the ITA procedure) and bound styrene as part of a continuous series of analyses. Overall, the present ASTM extraction procedure using ethanol-toluene azeotrope is less satisfactory than the other procedures.

Some additional work on the ITA procedure may be desirable to see if more complete extraction can be obtained. Further work is needed on additional samples containing mixed acids or rosin acid alone to determine whether the presence of the latter causes the peculiar results observed here in the analysis of AC samples.

The authors are indebted to the Firestone Synthetic Rubber and Latex Company, Goodrich-Gulf Chemicals, Inc., and the Phillips Petroleum Company Copolymer Plant for their cooperation in preparing the samples used in the work on SBR, and to the Witco Chemical Company for providing sodium and aluminum soaps of known composition used in the designed experiments. The assistance of John Mandel and Mary N. Steel of the National Bureau of Standards in performing the statistical analyses is gratefully acknowledged.

9. References

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Table 1. Samples

<u>Samples</u>	<u>Type of Organic Acid</u>	<u>Type of Stabilizer^{1/}</u>	<u>Approx. Bound Styrene Content %</u>	<u>Source of Sample</u>
F-1 SA, F-1 AC	Fatty acid	PBNA	25	Firestone Synthetic Rubber and Latex Co.
F-2 SA, F-2 AC	"	BLE	3	
GG-1 SA, GG-1 AC	"	PBNA	23	Goodrich-Gulf Chemicals, Inc.
GG-2 SA, GG-2 AC	"	Stalite	44	
GG-1N SA, GG-1N AC	"	PBNA	23	
GG-1N SA, GG-2N AC	"	Stalite	44	
PP-1 SA, PP-1 AC	50:50 Fatty acid:	--	--	Phillips Petroleum Company, Copolymer Plant
PP-2 SA, PP-2 AC	Rosin acid	--	--	

^{1/} PBNA - phenyl-β-naphthylamine
 BLE - reaction product of acetone and diphenylamine
 Stalite - mixed alkylated diphenylamines

Table 2. Analysis of rubbers for organic acid and soap

<u>Sample</u>	<u>Complete-solution</u>		<u>ITA Extraction</u>		<u>ETA Extraction</u>	
	<u>Organic acid</u> %	<u>Soap</u> %	<u>Organic acid</u> %	<u>Soap</u> %	<u>Organic acid</u> %	<u>Soap</u> %
F-1 SA	4.98	0.56	4.84	0.50	4.83	0.36
F-2 SA	4.80	0.00	4.51	0.00	4.57	0.00
GG-1 SA	5.05	0.07	4.90	0.07	4.89	0.07
GG-2 SA	3.73	1.54	3.73	0.93	3.60	0.32
GG-1N SA	3.70	1.47	3.72	1.52	3.74	1.50
GG-2N SA	3.71	1.38	3.60	1.11	3.63	1.30
PP-1 SA	5.40	1.02	5.37	0.73	5.33	0.75
PP-2 SA	6.25	0.62	6.29	0.46	6.14	0.48

Table 3. Comparison of differences with standard error of differences^{1/}

<u>Sample</u>	<u>Organic Acid</u>		<u>Soap</u>	
	<u>CS-ITN</u>	<u>CS-ETA</u>	<u>CS-ITA</u>	<u>CS-ETA</u>
F-1 SA	0.138	0.156	0.058	0.198
	0.042	0.035	0.028	0.026
F-2 SA	0.290	0.233	0.000	0.000
	0.044	0.040	0.028	0.028
GG-1 SA	0.143	0.153	-0.007	0.000
	0.044	0.040	0.028	0.028
GG-2 SA	0.000	0.127	0.611	1.218
	0.038	0.035	0.026	0.026
GG-1N SA	-0.023	-0.037	-0.050	-0.030
	0.044	0.040	0.028	0.028
GG-2N SA	0.105	0.077	0.277	0.083
	0.045	0.040	0.028	0.028
PP-1 SA	0.035	0.078	0.290	0.273
	0.038	0.030	0.026	0.023
PP-2 SA	-0.044	0.106	0.161	0.136
	0.039	0.032	0.026	0.024

^{1/} Upper value for each sample is the difference; the lower value is the standard error computed by the following general formula:

$$\sigma \text{ diff} = \sqrt{\frac{\sigma_A^2}{n_1} + \frac{\sigma_B^2}{n_2}}$$

where σ_A^2 and σ_B^2 were estimated as pooled variances from all the sets of replicate values for each method, and n_1 and n_2 are the number of replicates for methods A and B, respectively, for the sample considered.

Table 4. Comparison of complete-solution and ITA extraction procedures for soap in SA samples

<u>Sample</u>	<u>Soap</u>	
	<u>Complete- solution</u> %	<u>ITA extraction</u> %
F-2 SA	0.00	0.00
GG-1 SA	0.07	0.07
Solprene 1205	0.44	0.30
F-1 SA	0.56	0.50
PP-2 SA	0.62	0.46

Table 5. Analysis of rubbers, serums, washes, and latexes

Sample	Latex Organic acid %	Total organic acid in rubber, wash, and serum ^{1/}		
		Complete-solution %	ITA %	ETA %
F-1 SA	5.70	5.52	5.32	5.18
F-1 AC		5.70	5.33	4.96
F-2 SA	<u>2/</u>	4.85	4.56	4.62
F-2 AC-		4.85	4.49	3.85
GG-1 SA	5.27	5.11	4.98	4.97
GG-1 AC		5.88	4.92	4.45
GG-2 SA	5.38	5.16	4.59	3.90
GG-2 AC		6.22	4.80	4.38
GG-1N SA	5.16	5.06	5.13	5.13
GG-1N AC		5.66	5.14	4.94
GG-2N SA	5.17	5.06	4.68	4.90
GG-2N AC		5.51	5.03	4.97
PP-1 SA	6.62	6.52	6.20	6.21
PP-1 AC		5.66	4.66	3.89
PP-2 SA	6.61	6.87	6.72	6.61
PP-2 AC		6.69	5.63	3.95

^{1/} Data for each procedure usually include the traces of organic acid recovered from washes and serums added to that found in rubber, as well as organic acid as soap. The only exceptions are samples GG-1 SA, GG-1 AC, GG-2 SA, and GG-2 AC. Samples GG-1 SA and GG-1 AC were not washed, and the washes of samples GG-2 SA and GG-2 AC were inadvertently discarded. The serums of GG-1 AC and GG-2 AC were not tested. Since in practice the quantities involved are small, their absence should not vitiate the comparisons.

^{2/} Latex not available.

Table 6. Comparison of complete-solution and ITA extraction procedures for AC samples^{1/}

<u>Sample</u>	<u>Complete-solution</u> %	<u>ITA extraction</u> %
F-1 AC	+0.18	-0.19
F-2 AC	0.00	-0.36
GG-1 AC	+0.77	-0.19
GG-2 AC	+1.06	-0.36
GG-1N AC	+0.60	+0.08
GG-2N AC	+0.45	-0.03
PP-1 AC	-0.86	-1.86
PP-2 AC	-0.18	-1.24

^{1/} Values given are the percent of organic acid over and below the total organic acid determined by CS analysis of the respective SA rubbers, serums, and washes. (See Table 5)

Table 7. Comparison of methods of analysis for stabilizers and bound styrene

<u>Sample</u>	<u>Type of stabilizer</u>	<u>Stabilizer</u> ^{1/}		<u>Bound styrene</u> ^{2/}	
		<u>ITA</u> %	<u>ASTM</u> ^{1/} %	<u>ITA</u> %	<u>ASTM</u> %
F-1 SA	PBNA	1.21	1.22	24.5	24.6
F-1 AC	PBNA	1.22	1.24	24.6	25.6
F-2 SA	BLE	1.01	1.30	3.0	2.9
F-2 AC	BLE	.96	1.40	2.9	2.9
GG-1N SA	PBNA	1.54	1.54	23.5	23.3
GG-1N AC	PBNA	1.26	1.24	23.5	23.3
GG-2N SA	Stalite	1.22	1.29	44.2	44.2
GG-2N AC	Stalite	1.26	1.38	43.9	44.0

^{1/}ASTM D 1416, Sections 42-48, Method A(1).

^{2/}Samples extracted according to appropriate procedures given in this paper and in ASTM D 1416, Sections 25-29 (1).

Table 8. Comparison of thymol blue and meta-cresol purple for the titration of soap and organic acid in aqueous ITA

<u>Sample</u>	<u>Soap</u>		<u>Organic acid</u>	
	<u>TB</u> %	<u>MCP</u> %	<u>TB</u> %	<u>MCP</u> %
GG-1 SA	0.04	0.10	-	-
	.05	.05	-	-
GG-2 SA	-	-	3.72	3.67
F-2 SA	-	-	4.61	4.51
6608 P	.15	.22	-	-
	.15	.13	-	-
Solprene 1205	.30	.31	-	-
	.29	.29	-	-
PP-2 SA	.50	.51	5.40	5.39
PP-1 SA	.71	.74	6.31	6.27

Table 9. Study of systematic errors of titrations
(Relative and constant-type errors)

	<u>Sodium Stearate</u>	<u>Aluminum Stearate</u>	
		<u>Titration Range</u>	
		<u>Serums and Washes</u>	<u>Rubber</u>
		<u>Relative Error</u>	
Calculated slope	33.46 ml/g	33.25 ml/g	33.25 ml/g
Slope \underline{m} from st regression study	33.47 ml/g	33.68 ml/g	33.21 ml/g
Standard error of estimate of \underline{m}	0.22 ml/g	0.51 ml/g	0.07 ml/g
		<u>Constant Error</u>	
Solvent blank	0.022 ml	0.00 ml	0.00 ml
Intercept \underline{b} from regression study	-0.012 ml	-0.014 ml	-0.011 ml
Standard error of \underline{b}	-0.025 ml	0.010 ml	0.006 ml

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